

1           **PROCESS FOR THE PRODUCTION OF HIGH QUALITY MIDDLE**  
2       **DISTILLATES FROM MILD HYDROCRACKERS AND VACUUM GAS OIL**  
3       **HYDROTREATERS IN COMBINATION WITH EXTERNAL FEEDS IN THE**  
4       **MIDDLE DISTILLATE BOILING RANGE**

5  
6           **FIELD OF THE INVENTION**  
7

8       This invention is directed to processes for upgrading the fraction boiling in the  
9       middle distillate range which is obtained from VGO hydrotreaters or moderate  
10      severity hydrocrackers. This invention involves a multiple-stage process  
11      employing a single hydrogen loop.

12  
13           **BACKGROUND OF THE INVENTION**  
14

15      In the refining of crude oil, vacuum gas oil hydrotreaters and hydrocrackers  
16      are used to remove impurities such as sulfur, nitrogen, and metals from the  
17      crude oil. Typically, the middle distillate boiling material (boiling in the range  
18      from 250°F-735°F) from VGO hydrotreating or moderate severity  
19      hydrocrackers does not meet the smoke point, the cetane number or the  
20      aromatic specification. In most cases, this middle distillate is separately  
21      upgraded by a middle distillate hydrotreater or, alternatively, the middle  
22      distillate is blended into the general fuel oil pool or used as home heating oil.  
23      There are also streams in the diesel boiling range, from other units such as  
24      Fluid Catalytic Cracking, Delayed Coking and Visbreaking that require  
25      upgrading. Very often, existing diesel hydrotreaters are not designed to the  
26      pressure limits required to process these streams and the mild hydrocracking  
27      unit provides an opportunity for simultaneous upgrading of these streams.

28  
29      There have been some previously disclosed processes in which  
30      hydroprocessing occurs within a single hydroprocessing loop. International  
31      Publication No. WO 97/38066 (PCT/US97/04270), published October 16,  
32      1997, discloses a process for reverse staging in hydroprocessing reactor  
33      systems. This hydroprocessor reactor system comprises two reactor zones,

1 one on top of the other, in a single reaction loop. In the preferred  
2 embodiment, a hydrocarbon feed is passed to a denitrification and  
3 desulfurization zone, which is the lower zone. The effluent of this zone is  
4 cooled and the gases are separated from it. The liquid product is then passed  
5 to the upper zone, where hydrocracking or hydrotreating may occur. Deeper  
6 treating preferably occurs in the upper zone.

7

8 U.S. Pat. No. 5,980,729 discloses a configuration similar to that of  
9 WO 97/38066. A hot stripper is positioned downstream from the  
10 denitrification/desulfurization zone, however. Following this stripper is an  
11 additional hydrotreater. There is also a post-treat reaction zone downstream  
12 of the denitrification/desulfurization zone in order to saturate aromatic  
13 compounds. U.S. Pat. No. 6,106,694 discloses a similar configuration to that  
14 of U.S. Pat. No. 5,980,729, but without the hydrotreater following the stripper  
15 and the post-treat reaction zone.

16

17 SUMMARY OF THE INVENTION

18

19 With this invention, the middle distillate is hydrotreated in the same high  
20 pressure loop as the vacuum gas oil hydrotreating reactor or the moderate  
21 severity hydrocracking reactor, but the reverse staging configuration  
22 employed in the references is not employed in the instant invention. The  
23 investment cost saving and/or utilities saving involved in the use of a single  
24 hydrogen loop are significant since a separate middle distillate hydrotreater is  
25 not required. Other advantages include optimal hydrogen pressures for each  
26 step, as well as optimal hydrogen consumption and usage for each product.  
27 There is also a maximum yield of upgraded product, without the use of recycle  
28 liquid. The invention is summarized below.

29

30 A method for hydroprocessing a hydrocarbon feedstock, said method  
31 employing at least two reaction zones within a single reaction loop,  
32 comprising the following steps:

33

- 1    (a) passing a hydrocarbonaceous feedstock to a first hydroprocessing zone  
2       having one or more beds containing hydroprocessing catalyst, the  
3       hydroprocessing zone being maintained at hydroprocessing conditions,  
4       wherein the feedstock is contacted with catalyst and hydrogen;
- 5
- 6    (b) passing the effluent of step (a) directly to a hot high pressure separator,  
7       wherein the effluent is contacted with a hot, hydrogen-rich stripping gas  
8       to produce a vapor stream comprising hydrogen, hydrocarbonaceous  
9       compounds boiling at a temperature below the boiling range of the  
10      hydrocarbonaceous feedstock, hydrogen sulfide and ammonia and a  
11      liquid stream comprising hydrocarbonaceous compounds boiling  
12      approximately in the range of said hydrocarbonaceous feedstock;
- 13
- 14    (c) passing the vapor stream of step (b), after cooling and partial  
15       condensation, to a hot hydrogen stripper containing at least one bed of  
16       hydrotreating catalyst, where it is contacted countercurrently with  
17       hydrogen, while the liquid stream of step (b) is passed to fractionation;
- 18
- 19    (d) passing the overhead vapor stream from the hot hydrogen stripper of  
20       step (c), after cooling and contacting with water, the overhead vapor  
21       stream comprising hydrogen, ammonia, and hydrogen sulfide, along with  
22       light gases and naphtha to a cold high pressure separator, where  
23       hydrogen, hydrogen sulfide and light hydrocarbonaceous gases are  
24       removed overhead, ammonia is removed from the cold high pressure  
25       separator as ammonium bisulfide in the sour water stripper, and naphtha  
26       and middle distillates are passed to fractionation;
- 27
- 28    (e) passing the liquid stream from the hot hydrogen stripper of step (c) to a  
29       second hydroprocessing zone, the second hydroprocessing zone  
30       containing at least one bed of hydroprocessing catalyst suitable for  
31       aromatic saturation and ring opening, wherein the liquid is contacted  
32       under hydroprocessing conditions with the hydroprocessing catalyst, in  
33       the presence of hydrogen;

- 1       (f) passing the overhead from the cold high pressure separator of step (d)  
2              to an absorber, where hydrogen sulfide is removed before hydrogen is  
3              compressed and recycled to hydroprocessing vessels within the loop;  
4              and  
5  
6       (g) passing the effluent of step (e) to the cold high pressure separator of  
7              step (d).

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a hydroprocessing loop in which the post-treatment reactor is a middle distillate upgrader which operates at approximately the same pressure as the first stage reactor.

Figure 2 illustrates a hydroprocessing loop in which the post-treatment reactor is the same as that of Figure 1, but operates at lower pressure than the first stage reactor. A noble metal catalyst is used in the post-treatment reactor.

## DETAILED DESCRIPTION OF THE INVENTION

## 21 Description of the Preferred Embodiment

## 23 Description of Figure 1

25 Feed in stream 1 is mixed with recycle hydrogen and make-up hydrogen in  
26 stream 42. The feed has been preheated in a process heat exchanger train,  
27 as are the gas streams. The mixture of feed and gas, now in stream 34, is  
28 further heated using heat exchangers 43 and furnace 49. Stream 34 then  
29 enters the first stage downflow fixed bed reactor 2. The first bed 3 of reactor  
30 2 may contain VGO hydrotreater catalyst or a moderate severity hydrocracker  
31 catalyst. There may be a succession of fixed beds 3, with interstage quench  
32 streams, 4 and 5 delivering hydrogen in between the beds.

1 The effluent 6 of the first stage reactor 2, which has been hydrotreated and  
2 partially hydrocracked, contains hydrogen sulfide, ammonia, light gases,  
3 naphtha, middle distillate and hydrotreated vacuum gas oil. The effluent  
4 enters the hot high pressure separator or flash zone 8 at heavy oil reactor  
5 effluent conditions where part of the diesel and most of the lighter material is  
6 separated from the unconverted oil. The hot high pressure separator has a  
7 set of trays 44 with hydrogen rich gas introduced at the bottom for stripping  
8 through stream 46.

9

10 Stream 9 is primarily hydrotreated heavy gas oil, boiling at temperatures  
11 greater than 700°F. The valve 10 indicates that pressure is reduced before  
12 the unconverted oil is sent to the fractionation section in stream 11.

13

14 Stream 21 contains the overhead from the hot high pressure separator.  
15 Stream 21 is cooled in exchanger 22 (by steam generation or process heat  
16 exchange) before entering the hot hydrogen stripper/reactor 23. Stream 21  
17 flows downwardly through a bed of hydrotreating catalyst 52, while being  
18 contacted with countercurrent flowing hydrogen from stream 51.

19

20 The overhead stream 26 contains hydrogen, ammonia and hydrogen sulfide,  
21 along with light gases and naphtha. The differential operating pressure  
22 between the hot hydrogen stripper/reactor 23 and cold high pressure  
23 separator 17 is maintained by control valve 50. Stream 26 is cooled in  
24 exchanger 27 and joins stream 14 to form stream 16. Water is injected  
25 (stream 36) into the stream 16 to remove most of the ammonia as ammonium  
26 bisulfide solution (ammonia and hydrogen sulfide react to form ammonium  
27 bisulfide which is converted to solution by water injection). The stream is then  
28 air cooled by cooler 45. The stream 16 enters the cold high pressure  
29 separator 17. Hydrogen, light hydrocarbonaceous gases, and hydrogen  
30 sulfide are removed overhead through stream 19. Hydrogen sulfide is  
31 removed from the stream in the hydrogen sulfide absorber 20. Ammonia and  
32 hydrogen sulfide are removed with the sour water stream (not shown) from  
33 the cold high pressure separator 17.

1 Stream 40, which contains hydrogen-rich gas, is compressed in compressor  
2 30 and splits into streams 29 and 32. Stream 32 passes to the hot hydrogen  
3 stripper/reactor 23. Stream 31 is diverted from stream 29 for use as  
4 interstage quench. Streams 4 and 5 are diverted from stream 31. Stream 29,  
5 containing hydrogen, is combined with hydrogen stream 42 prior to combining  
6 with oil feed stream 1.

7

8 Make-up hydrogen 38 is compressed and sent to four separate locations,  
9 upstream of reactor 2 to combine with feed stream 1 (through stream 42), to  
10 the hot high pressure separator 8 through stream 46, to the hot hydrogen  
11 stripper/reactor through stream 51, and to the middle distillate upgrader  
12 (stream 35) to combine with recycle diesel or kerosene or to be used as  
13 interstage quench. Stream 38, containing make-up hydrogen, passes to the  
14 make-up hydrogen compressor 37. From stream 41, which exits compressor  
15 37 containing compressed hydrogen, streams 35, 42 and 46 are diverted.

16

17 The middle distillate upgrader 12 consists of one or more multiple beds 13 of  
18 hydrotreating/hydrocracking catalyst (such as Ni-Mo, Ni-W and/or noble  
19 metal) for aromatic saturation and ring opening to improve diesel product  
20 qualities such as aromatic level and cetane index. In the embodiment of  
21 Figure 1, the middle distillate upgrader is operated at approximately the same  
22 pressure as the first stage reactor 2. Quench gas (stream 47) may be  
23 introduced in order to control reactor temperature. Stream 24 may be  
24 combined with recycle diesel or kerosene (stream 48) from the fractionator  
25 when no other external feeds (stream 7) are to be processed and cooled in  
26 exchanger 25. Hydrogen from stream 35 is combined with stream 24 prior to  
27 entering the middle distillate upgrader 12. Stream 24 enters the reactor at the  
28 top and flows downwardly through the catalyst beds 13.

29

30 Stream 14, which is the effluent from the middle distillate upgrader 12, is used  
31 to heat the other process streams in the unit (see exchanger 15) and then  
32 joins with stream 26 to form stream 16, which is sent to the effluent air cooler  
33 and then to the cold high-pressure separator 17. Water is continuously

1 injected into the inlet piping of the effluent air cooler to prevent the deposition  
2 of salts in the air cooler tubes. In the cold high pressure separator 17,  
3 hydrogen, hydrogen sulfide and ammonia leave through the overhead stream  
4 19, while naphtha and middle distillates exit through stream 18 to fractionation  
5 (stream 39).

6

## 7 **Description of Figure 2**

8

9 As described in Figure 1, feed in stream 1 is mixed with recycle hydrogen and  
10 make-up hydrogen in stream 42. The feed has been preheated in a process  
11 heat exchange train as are the gas streams. The mixture of feed and gas,  
12 now in stream 34, is further heated using heat exchangers 43 and furnace 51.  
13 Stream 34 then enters the first stage downflow fixed bed reactor 2. The first  
14 bed 3 of reactor 2 may contain VGO hydrotreater catalyst or a moderate  
15 severity hydrocracker catalyst. There may be a succession of fixed beds 3,  
16 with interstage quench streams, 4 and 5 delivering hydrogen in between the  
17 beds.

18

19 The effluent 6 of the first stage reactor, which has been hydrotreated and  
20 partially hydrocracked, contains hydrogen sulfide, ammonia, light gases,  
21 naphtha, middle distillate and hydrotreated vacuum gas oil. The effluent  
22 enters the hot high pressure separator or flash zone 8 at heavy oil reactor  
23 effluent conditions where part of the diesel and most of the lighter material is  
24 separated from the unconverted oil. The hot high pressure separator has a  
25 set of trays 44 with hydrogen rich gas introduced at the bottom for stripping  
26 through stream 46.

27

28 Stream 9 is primarily hydrotreated heavy gas oil, boiling at temperatures  
29 greater than 700°F. The valve 10 indicates that pressure is reduced before  
30 the unconverted oil is sent to the fractionation section in stream 11.

31

32 Stream 21 contains the overhead from the hot high pressure separator and  
33 may be joined by external feed 7. Stream 21 is then cooled in exchanger 22

1 (by steam generation or process heat exchange) before entering the hot  
2 hydrogen stripper/reactor 23. Stream 21 flows downwardly through a bed of  
3 hydrotreating catalyst 52, while being contacted with countercurrent flowing  
4 hydrogen from stream 32.

5

6 The overhead stream 26 from hot hydrogen stripper/reactor 52 contains  
7 hydrogen, ammonia and hydrogen sulfide, along with light gases and  
8 naphtha. It is cooled in exchanger 27. Water is injected (stream 36) into the  
9 stream 26 to remove most of the ammonia as ammonium bisulfide solution  
10 (ammonia and hydrogen sulfide react to form ammonium bisulfide which is  
11 converted to solution by water injection). The stream is then air cooled by  
12 cooler 45. The effluent from the air cooler enters the cold high pressure  
13 separator 17. Hydrogen, light hydrocarbonaceous gases, and hydrogen  
14 sulfide are removed overhead through stream 19. Hydrogen sulfide is  
15 removed (stream 51) from the stream in the hydrogen sulfide absorber 20.  
16 Ammonia and hydrogen sulfide is removed with the sour water stream  
17 (stream 48) from the cold high pressure separator 17. Stream 40, which  
18 contains hydrogen, is compressed in compressor 30 and splits into streams  
19 29 and 31. Stream 31 is diverted from stream 29 for use as interstage  
20 quench. Streams 4 and 5 are diverted from stream 31. Stream 29, containing  
21 hydrogen, is combined with hydrogen stream 42 prior to combining with oil  
22 feed stream 1.

23

24 Make-up hydrogen 38 is compressed and sent to four separate locations,  
25 upstream of reactor 2 to combine with feed stream 1 (through stream 42), to  
26 the hot high pressure separator 8 through stream 46, to the hot hydrogen  
27 stripper/reactor 23, and to the middle distillate upgrader (stream 35) to  
28 combine with recycle diesel or kerosene or to be used as interstage quench.  
29 Stream 38, containing make-up hydrogen, passes to the make-up hydrogen  
30 compressor 37. From stream 41, which exits compressor 37 containing  
31 compressed hydrogen, streams 35, 42 and 46 are diverted.

32

1 In this embodiment, the middle distillate upgrading reactor 12 operates at  
2 lower pressure than the first stage reactor 2. Liquid (stream 24) from the hot  
3 hydrogen stripper 52 is reduced in pressure (via valve 28) and is combined  
4 with make-up hydrogen (stream 35) after the second stage of compression of  
5 the make-up hydrogen compressor 37. Recycle kerosene or diesel (stream  
6 50) may be added at this point. The mixture is sent after preheat (in  
7 exchanger 25) to the middle distillate upgrader 12, which is preferably loaded  
8 with one or more beds of noble metal catalyst 13. Part of the make-up  
9 hydrogen is available as quench (stream 47) between the beds for multiple  
10 bed application. Reactor effluent (stream 14) is cooled in a series of heat  
11 exchangers 15 and sent to a cold high pressure separator 49.

12

13 Overhead vapor 38 from the cold high pressure separator 49 is essentially  
14 high-purity hydrogen with a small amount of hydrocarbonaceous light gases.  
15 The vapor is sent to the make-up hydrogen compressor 37. Compressed  
16 make-up hydrogen (stream 29) is sent to the high pressure reactor 2, the high  
17 pressure separator 8, and hot hydrogen stripper/reactor 23. Bottoms (stream  
18 18) from the cold high-pressure separator 17 is sent to the fractionation  
19 section (stream 53) after pressure reduction.

20 Stream 14, which is the effluent from the middle distillate upgrader 12, is used  
21 to heat the other process streams in the unit (see exchanger 15) and passes  
22 to the cold high pressure separator 49. The liquid effluent of cold high  
23 pressure separator 49, stream 39, passes to fractionation.

24

#### 25 Feeds

26

27 A wide variety of hydrocarbon feeds may be used in the instant invention.  
28 Typical feedstocks include any heavy or synthetic oil fraction or process  
29 stream having a boiling point above 300°F (150°C). Such feedstocks include  
30 vacuum gas oils, heavy atmospheric gas oil, delayed coker gas oil, visbreaker  
31 gas oil, demetallized oils, vacuum residua, atmospheric residua, deasphalting  
32 oil, Fischer-Tropsch streams, FCC streams, etc.

1 For the first reaction stage, typical feeds will be vacuum gas oil, heavy coker  
2 gas oil or deasphalting oil. Lighter feeds such as straight run diesel, light cycle  
3 oil, light coker gas oil or visbroken gas oil can be introduced upstream of the  
4 hot hydrogen stripper/reactor 23.

5

6 Products

7

8 Figures 1 and 2 depict two different versions of the instant invention, directed  
9 primarily to high quality middle distillate production as well as to production of  
10 heavy hydrotreated gas oil.

11

12 The process of this invention is especially useful in the production of middle  
13 distillate fractions boiling in the range of about 250°F-700°F (121°C-371°C). A  
14 middle distillate fraction is defined as having a boiling range from about 250°F  
15 to 700°F. At least 75 vol%, preferably 85 vol%, of the components of the  
16 middle distillate have a normal boiling point of greater than 250°F. At least  
17 about 75 vol%, preferably 85 vol%, of the components of the middle distillate  
18 have a normal boiling point of less than 700°F. The term "middle distillate"  
19 includes the diesel, jet fuel and kerosene boiling range fractions. The  
20 kerosene or jet fuel boiling point range refers to the range between 280°F and  
21 525°F (138°C-274°C). The term "diesel boiling range" refers to hydrocarbons  
22 boiling in the range from 250°F to 700°F (121°C-371°C).

23

24 Gasoline or naphtha may also be produced in the process of this invention.  
25 Gasoline or naphtha normally boils in the range below 400°F (204°C), or C<sub>5</sub>-.  
26 Boiling ranges of various product fractions recovered in any particular refinery  
27 will vary with such factors as the characteristics of the crude oil source, local  
28 refinery markets and product prices.

29

30 Heavy diesel, another product of this invention, usually boils in the range from  
31 550°F to 750°F.

32

1    Conditions

2  
3    Hydroprocessing conditions is a general term which refers primarily in this  
4    application to hydrocracking or hydrotreating, preferably hydrocracking. The  
5    first stage reactor, as depicted in Figures 1 and 2, may be either a VGO  
6    hydrotreater or a moderate severity hydrocracker.

7

8    Hydrotreating conditions include a reaction temperature between 400°F-900°F  
9    (204°C-482°C), preferably 650°F-850°F (343°C-454°C); a pressure from 500  
10   to 5000 psig (pounds per square inch gauge) (3.5-34.6 MPa), preferably 1000  
11   to 3000 psig (7.0-20.8 MPa); a feed rate (LHSV) of 0.5 hr<sup>-1</sup> to 20 hr<sup>-1</sup> (v/v); and  
12   overall hydrogen consumption 300 to 5000 scf per barrel of liquid hydrocarbon  
13   feed (53.4-356 m<sup>3</sup>/m<sup>3</sup> feed).

14

15   In the embodiment shown in Figure 1, the first stage reactor and the middle  
16   distillate upgrader are operating at the same pressure. In the embodiment  
17   shown in Figure 2, the middle distillate upgrader is operating at a lower  
18   pressure than the first stage reactor.

19

20   Typical hydrocracking conditions include a reaction temperature of from  
21   400°F-950°F (204°C-510°C), preferably 650°F-850°F (343°C-454°C).  
22   Reaction pressure ranges from 500 to 5000 psig (3.5-34.5 MPa), preferably  
23   1500 to 3500 psig (10.4-24.2 MPa). LHSV ranges from 0.1 to 15 hr<sup>-1</sup> (v/v),  
24   preferably 0.25-2.5 hr<sup>-1</sup>. Hydrogen consumption ranges from 500 to 2500 scf  
25   per barrel of liquid hydrocarbon feed (89.1-445 m<sup>3</sup> H<sub>2</sub>/m<sup>3</sup> feed).

26

27   Catalyst

28

29   A hydroprocessing zone may contain only one catalyst, or several catalysts in  
30   combination.

31

32   The hydrocracking catalyst generally comprises a cracking component, a  
33   hydrogenation component and a binder. Such catalysts are well known in the

1 art. The cracking component may include an amorphous silica/alumina phase  
2 and/or a zeolite, such as a Y-type or USY zeolite. Catalysts having high  
3 cracking activity often employ REX, REY and USY zeolites. The binder is  
4 generally silica or alumina. The hydrogenation component will be a Group VI,  
5 Group VII, or Group VIII metal or oxides or sulfides thereof, preferably one or  
6 more of molybdenum, tungsten, cobalt, or nickel, or the sulfides or oxides  
7 thereof. If present in the catalyst, these hydrogenation components generally  
8 make up from about 5% to about 40% by weight of the catalyst. Alternatively,  
9 platinum group metals, especially platinum and/or palladium, may be present  
10 as the hydrogenation component, either alone or in combination with the base  
11 metal hydrogenation components molybdenum, tungsten, cobalt, or nickel. If  
12 present, the platinum group metals will generally make up from about 0.1% to  
13 about 2% by weight of the catalyst.

14

15 Hydrotreating catalyst, if used, will typically be a composite of a Group VI  
16 metal or compound thereof, and a Group VIII metal or compound thereof  
17 supported on a porous refractory base such as alumina. Examples of  
18 hydrotreating catalysts are alumina supported cobalt-molybdenum, nickel  
19 sulfide, nickel-tungsten, cobalt-tungsten and nickel-molybdenum. Typically,  
20 such hydrotreating catalysts are presulfided.

21

1 Example

2

3

## POLYHYDROXYLATION OF MILD HYDROCARBON

## 4 DISTILLATES FOR CETANE UPGRADING

Feed	Mild Hydrocracked Distillate from Vacuum Gas Oil/Coker Gas Oil Blend	Mild Hydrocracked Distillate from Middle Eastern Vacuum Gas Oil
Mild Hydrocracking Conversion	30 Liquid Volume % <680°F	31 Liquid Volume % <700°F
Hydrotreating Catalyst	Noble metal/Zeolite	Base metal/Alumina
Hydrotreating Conditions:		
Catalyst Bed Temperature, °F	594	720
LHSV, 1/hr	1.5	2.0
Gas/Oil Ratio, SCF/B	3000	5000
H <sub>2</sub> Partial Pressure, psia	800	1900
Cetane Uplift (typical)	7 to 15	2 to 7

5

- 6 The Table above illustrates the effectiveness of upgrading the effluent of the  
7 first stage reactor, which has been mildly hydrocracked. The effluent is  
8 hydrotreated in the middle distillate upgrader. Cetane uplift (improvement) is  
9 greater, and at less severe conditions, using a catalyst having a noble metal  
10 hydrogenation component with a zeolite cracking component than when using  
11 a catalyst having base metal hydrogenation components on alumina, an  
12 amorphous support. Cetane uplift can be higher if external diesel range feeds  
13 (7) are added upstream of Hot High Pressure Separator 44.